Carbon nano-tubes in improving the mechanical property of cement-based composite materials

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ABSTRACT. Carbon nano-tubes as a kind of novel nanometer material have been extensively applied in cement-based composite materials to improve their properties. This study prepared carbon nano-tubes cement based composite materials by evenly scattering carbon nano-tubes in cement materials using ultrasonic method and emphatically investigation the improvement of the mechanical property. The results demonstrated that, the addition of carbon nano-tubes could significantly relieve the mechanical properties of cement based composite materials. When the mixing amount of carbon nano-tubes reached the optimal value, i.e., 0.1%, the improvement of the mechanical property of the carbon nano-tubes cement based composite materials was the best. The microstructure analysis using scanning electron microscope suggested that, carbon nano-tubes produced bridging and pullout effects in the cement-based materials, which enhanced the damage resistance of the cement based materials.

KEYWORDS. Carbon nano-tubes; Cement-based composite material; Mechanical property.

OPEN ACCESS

Citation: Wu, X., Dai, L., Carbon nano-tubes in improving the mechanical property of cement-based composite materials, Frattura ed Integrità Strutturale, 41 (2017) 388-395.

Received: 11.04.2017
Accepted: 15.05.2017
Published: 01.07.2017

INTRODUCTION

With the rapid development of modern society, requirements for the mechanical property of cement concrete whose demand is the largest and which is the most widely used construction material has become stricter and stricter. The traditional cement materials have been far from enough to satisfy the requirements on material properties in special occasions such as earthquake and temperature stress effect in dam body. How to improve the mechanical property of cement concrete and then perform effective test has been an issue concerned by the world [1].
Relevant studies [2-4] suggested that, the addition of an appropriate amount of carbon materials in cement base can not only enhance the mechanical property and crack resistance, but also impart a favorable voltage-sensitive property. Carbon nano-tubes, a kind of tubular nano carbon material containing graphite crystal, has nearly perfect mechanical performance compared to the traditional carbon fibres. It is the fibre material with the best comprehensive performance so far. Carbon nano-tubes can be typed into single-wall carbon nano-tubes and multiple-wall carbon nano-tubes according to the layers of

carbon atoms. Single-wall carbon nano-tubes which was expensive is generally applied in the fields of field emission panel display and sensors. Multiple-wall carbon nano-tubes which is low in cost and has achieved scale production and extensive application is usually applied in the study of reinforced composite materials. Base materials such as polymer base, metal base and ceramic base are frequently studied, while few studies concern cement-based composite materials [5-9].

In 2003, Campillo I. et al. [10] from Spain reported the reinforcement of cement-based composite materials using carbon nano-tubes for the earliest and found single-wall carbon nano-tubes and multiple-wall carbon nano-tubes could improve the compressive strength of cement paste for 6% and 30% respectively in 14 days and that effective control of the structure of multiple-wall carbon nano-tubes in cement base could significantly enhance its strength. In 2008, Kowald T. et al. [11] from Suegen in Germany investigated the effects of unprocessed and oxidized multiple-wall carbon nano-tubes on cement hydration products taking pure C_3S as the simplified model system as well as the effects of multiple-wall carbon nano-tubes on the micro-mechanical properties of cement hydration products using nanoindentation technology. The unprocessed multiple-wall carbon nano-tubes increased the number of low-density C-S-H in composite materials and oxidized multiple-wall carbon nano-tubes increased the high-density C-S-H. They also pointed out that multiple-wall carbon nano-tubes could enhance the performance of ultra high performance concrete as the regulation phase of cement hydration product. Since 2008, studies on carbon nano-tubes cement-based composite materials has began around the world. Luo J.L. et al. [12] analyzed the correlation between the electrical resistivity of carbon nano-tubes cement-based composite materials and the mixing amount of carbon nano-tubes and further analyzed its voltage-sensitive property. Morsy M.S. et al. [13] found adding multi-walled carbon nano-tubes whose mass was 0.02% that of cement could enhance its compressive strength.

For material researchers, it is urgent to study on the application of carbon nano-tubes in cement-based materials.The breakthrough of production and application of carbon nano-tubes are bound to motivate the development of nanotechnology and the emergence of related high-tech industries, which may induce a new scientific reformation and bring huge benefits to the whole society. In this study, carbon nano-tubes were evenly scattered in water solution by ultrasonic method using cetyl trimethyl ammonium bromide (CTAB), and then the solution was added into cement paste to investigate mechanical and endurance performance of the carbon nano-tubes cement-based composite materials.

TEST PROFILE

Raw materials for test

Carbon nano-tubes which was prepared by chemical vapor deposition and purchased from a nanometer material enterprise in Shandong, China was used; its physical parameters are shown in Tab. 1, and the structure diagram is shown in Fig. 1. P·O 42.5 ordinary Portland cement produced by Qingdao, Shandong, China was used, and its physical properties and mineral composition are shown in Tab. 2. CTAB, white chemical powder, was used. The water reducing agent used was polycarboxylate superplasticizer (solid content: 20%; water-reducing rate: 30%; Jiangsu Bote New Material Co., Ltd., China).

Purity/%	External diameter/nm	Length/μm	Specific surface area/(m^2/g)	Ash content/%	Electric conductivity/(s/cm)	-COOH content/%
>95	10-20	10-30	40-300	<1.5	100-1000	2.00

Table 1: The basic physical parameters of carbon nano-tubes.

Specific surface area/(m^2/Kg)	Setting time/min		Stability	Rupture strength/MPa		Compressive strength/MPa		Mineral composition/%				
	Initial set	Final set		3d	28d	3d	28d	C_3S	C_2S	C_3A	C_4AF	SO_3
330	191	247	Qualified	5.2	8.1	31.2	65.2	48.12	24.03	9.88	11.02	2.24

Table 2: The physical properties and mineral composition of the cement.

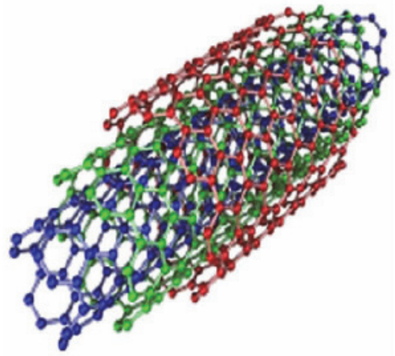

Figure 1: The schematic diagram of carbon nano-tubes structure.

Specimen moulding and testing

Carbon nano-tubes were added into the solution of CTAB. The mass ratio of CTAB to carbon nano-tubes was 10:1. Ultrasonic dispersion processing was performed using a ultrasonic apparatus, for 60 min, to ensure carbon nano-tubes evenly distributing in the water solution to form carbon nano-tubes suspension. Then the carbon nano-tubes suspenion was poured into a cement mixer along with the cement; the water cement ratio was 0.30. The stirring lasted for 6 min; the ratio of duration of stirring at the low speed to duration of stirring at the high speed was 2:1. The mixture of carbon nano-tubes and cement paste in the mixing pot was rapidly poured into a standard test mould in a specification of 40mm×40 mm×160 mm and another one in a specification of 40 mm×40 mm×40 mm at the end of stirring. It was vibrated to be dense mechanically. The moulds were removed after 24-h standard maintenance. Each test specimen was numbered and then put into water at the temperature of (20±1) □ for maintenance [14-16]. The mix proportion of the test specimens and the mixing amount are shown in Tab. 3. The microstructures of some specimens are shown in Fig. 2.

Sample	Water to cement ratio (W/C)	Mix proportion/wt%		
		MWCNTs	CTAB	Water reducer
No.0	0.30	0	0	0.1
No.1	0.30	0.05	0.5	0.1
No.2	0.30	0.10	1.0	0.1
No.3	0.30	0.15	1.5	0.1
No.4	0.30	0.20	2.0	0.1
No.5	0.30	0.25	2.5	0.1

Table 3: The mix proportion of carbon nano-tubes cement-based composite materials

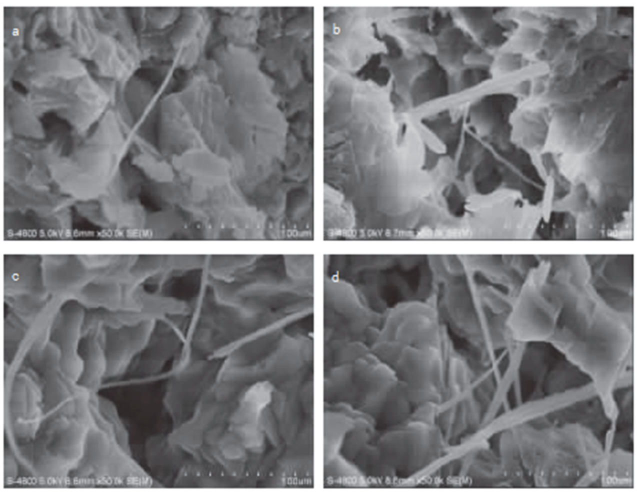

Figure 2: The microstructures of some specimens (the mixing amount of multiple-wall carbon nano-tubes in (a) - (d) is 0.05%, 0.1%, 0.2% and 0.25% respectively).

Property characterization

Effects of carbon nano-tubes on the bending strength of cement-based composite materials were investigated by performing a bending strength test with a DKZ-5000 antifracture test machine based on method of testing cements-determination of strength GB/T 17671-1999 which was formulated according to ISO 679:1989 (cement testing method - strength determination) whose main content is completely consistent with ISO 769; but some points of GB/T 17671-1999 were modified according to the actual condition of China, and the comprehensive strength testing results based on GB/T 17671-1999 are equal to those based on ISO 679:1989. Effects of carbon nano-tubes on the compressive strength of cement-based composite materials were investigated by performing a compressive strength test with a WHY microprocessor controlled fully automatic press machine. The morphology of carbon nano-tubes cement-based composite materials was characterized using a SU-70 thermal field emission scanning electron microscope, and the mechanism of interaction between carbon nano-tubes and cement was initially explored.

RESULT DISCUSSION

Mechanical properties

The testing results of the mechanical properties of carbon nano-tubes cement-based composite materials after seven days of maintenance are shown in Fig. 3. Fig. 3 suggests that, the bending and compressive strength of carbon nano-tubes cement-based composite materials was significantly improved compared to the blank group, 10% mostly. When the mixing amount of carbon nano-tubes was 0.10 wt% that of cement, the bending strength improved for 25.36%, i.e., 6.96 MPa, and the compressive strength improved for 21.8%, i.e., 40.94 MPa. The variation tendencies of bending and compressive strength of the test specimens were the same, increasing at first and decreasing after reaching the maximum value. It could be concluded that a small amount of carbon nano-tubes could produce a great influence on the mechanical properties of cement-based composite materials, but the changes in the strength were little when the mixing amount of carbon nano-tubes exceeded a certain value, i.e., excessive carbon nano-tubes might reduce the compressive and bending strength instead of improving the strength.

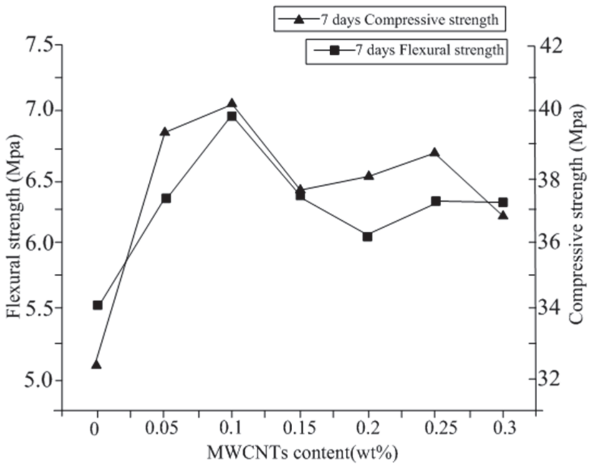

Figure 3: Mechanical properties of cement-based composite materials test specimens which were mixed with different amount of carbon nano-tubes after seven days of maintenance.

The testing results of the mechanical properties of carbon nano-tubes cement-based composite materials after 14 days of maintenance are shown in Fig. 4. Fig. 4 demonstrates there were changes in the variation tendencies of the bending and compressive strength of the test specimens; the bending strength fluctuated greatly with the increase of carbon nano-tubes amount, increasing first and then decreasing. The optimal values of the bending and compressive strength of cement-based composite materials were different. When the mixing amount of carbon nano-tubes was 0.10% that of cement, the bending strength reached the maximum value, 8.14 MPa, suggesting an improvement of 15.67%. When the mixing amount of carbon nano-tubes was 0.15%, the compressive strength reached the maximum value, 58.27 MPa, suggesting an improvement of 17.59%.

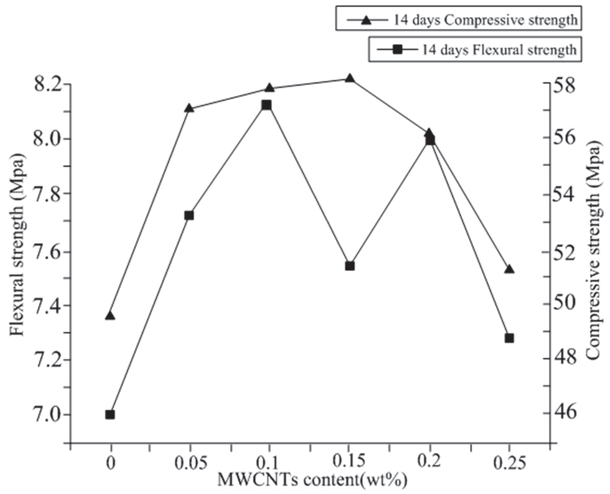

Figure 4: The mechanical properties of cement-based composite materials test specimens which were mixed with different amount of carbon nano-tubes after 14 days of maintenance.

The testing results of the mechanical properties of carbon nano-tubes cement-based composite materials after 14 days of maintenance are shown in Fig. 5. Fig. 5 shows that the compressive and bending strength of carbon nano-tubes cement-based composite materials was significantly improved (10% mostly) compared to the blank group after 28 days of maintenance. When the mixing amount of carbon nano-tubes was 0.10% that of cement, the bending strength reached the maximum value, 9.07 MPa, which was 12.56% higher than the blank controls. When the mixing amount of carbon nano-tubes was 0.05%, the compressive strength reached the maximum value, 72.44 MPa, suggesting an improvement of 13.01%. When the mixing amount of carbon nano-tubes was 0.10wt%, the variation of the compressive strength was not obvious but the variation of the bending strength was. The variation tendencies of the compressive and bending strength changed. The bending strength fluctuated significantly with the increase of carbon nano-tubes amount, increasing first and then decreasing. Regardless of No.0 blank sample, the curve showed unilateral slow drop.

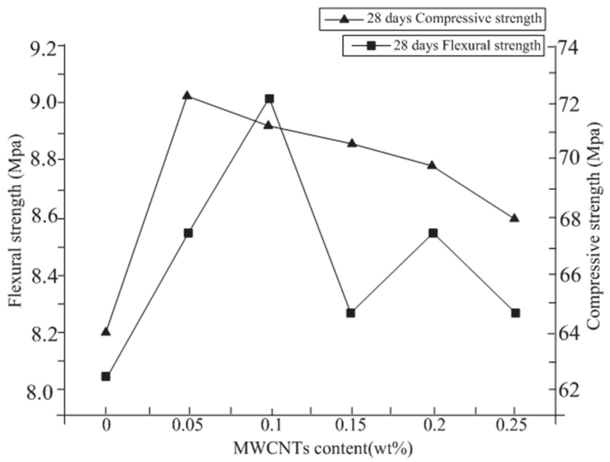

Figure 5: The mechanical properties of cement-based composite materials test specimens which were mixed with different amount of carbon nano-tubes after 28 days of maintenance.

The variation of the compressive and bending strength of the cement-based composite material test specimens which were mixed with different amount of carbon nano-tubes following the changes of age is shown in Fig. 6 and 7. The two figures demonstrated that the compressive and bending strength of the test specimens which was mixed with carbon nano-tubes tended to increase with the changes of age, and the increase amplitude decreased progressively. When the mixing amount of carbon nano-tubes was 0.10%, the improvement of the bending strength was optimal; the bending strength of the aforementioned test specimen was 9.07 MPa after 28 days of maintenance, which was 12.56% higher than that of the blank test specimen. As to the compressive strength, the cement-based composite material test specimen whose content of carbon nano-tubes was 0.05% was the best (72.44MPa), suggesting an improvement of 13.01% after 28 days of maintenance. The improvement of the compressive and bending strength was obvious in the early stage, which indicated carbon nano-tubes could effectively improve the strength of cement in the early stage. With the changes of carbon nano-tubes amount, the compressive and bending strength of the test specimens showed similar tendencies, i.e., increasing first and then decreasing, but the fluctuation of the bending strength was more obvious. According to the results after 7, 14 and 21 days of maintenance, the improvement of the compressive and bending strength was better when the mixing amount of carbon nano-tubes was 0.10%.

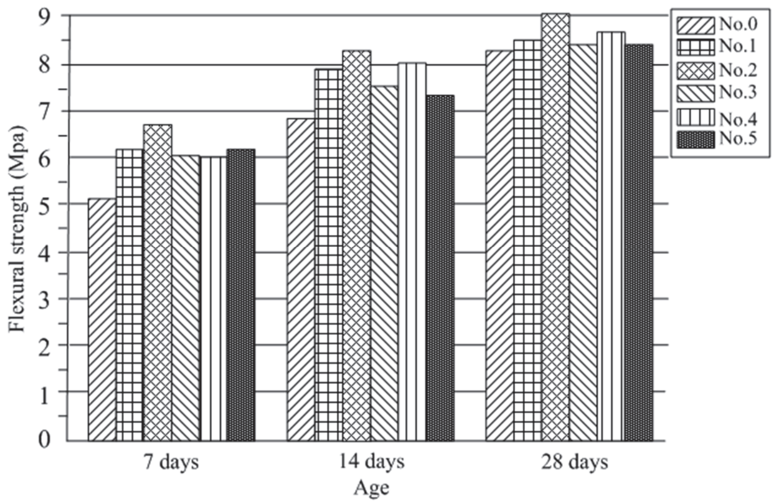

Figure 6: The variation of the bending strength of carbon nano-tubes cement-based composite materials test specimens along with the change of age.

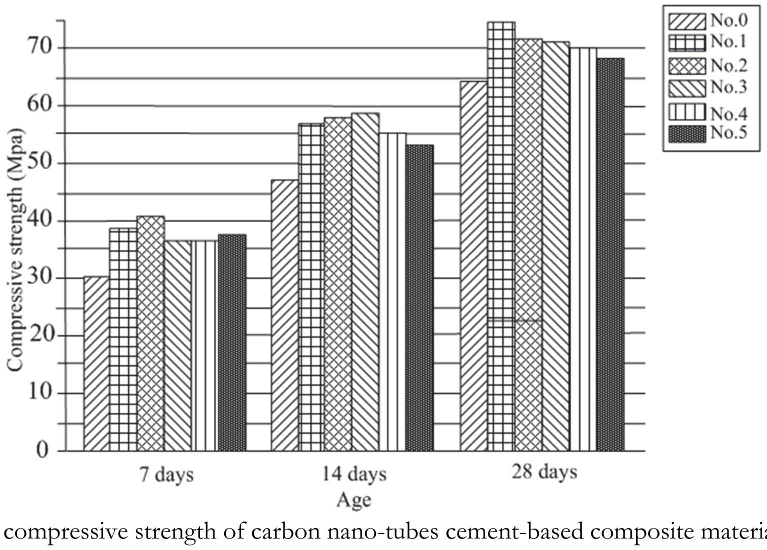

Figure 7: The variation of the compressive strength of carbon nano-tubes cement-based composite materials test specimens along with the change of age.

Analysis using scanning electron microscope

To further verify the mechanism of carbon nano-tubes in enhancing the mechanical properties of cement-based composite materials, the cross surface of the product was analyzed using a scanning electron microscope (SEM); the results are shown in Fig. 8. As shown in Fig. 8, carbon nano-tubes play a bridging role in the cement base. Because of the bridging effect, carbon nano-tubes could bear certain external force and consume external stress damages, which could help inhibiting the further growth of cracks and enhance the strength and toughness of the composite materials. With the growth of crack size or the increase of tensile stress, carbon nano-tubes could inhibit the expansion of cracks and shoulder most of external force. If local fracture occurred, a long and thin carbon tube would form at the fracture site of the cement material, and moreover carbon tubes would consume part of energy in the form of energy consumption in pullout, which could help improving breaking energy and overcoming fragility.

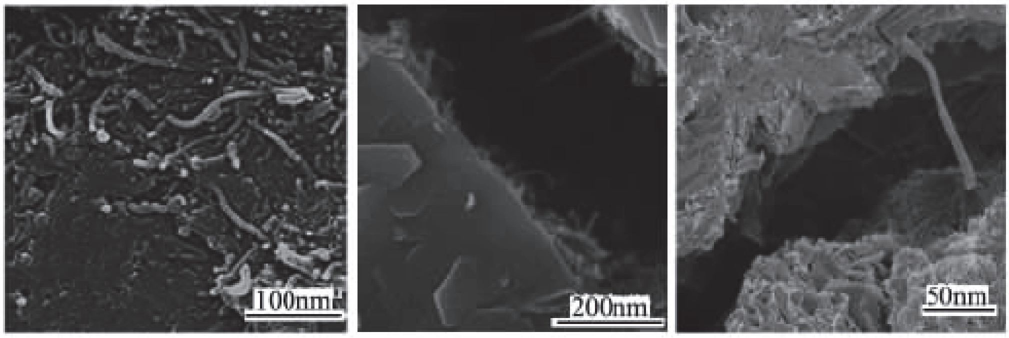

Figure 8: The observation results of carbon nano-tubes under a SEM.

CONCLUSIONS

The mixing of a certain amount of carbon nano-tubes can enhance the mechanical properties of cement-based composite materials. After analyzing the condition in the 7th, 14th and 28th d, it was found that the mixing of 0.10 wt% carbon nano-tubes had the best effect in improving the mechanical properties of cement-based composite materials; the bending and compressive strength improved for 12% approximately.

In the analysis using SEM, it was found that, carbon nano-tubes produced bridging and pullout effects in the cement-based materials and absorbed more damage energy to ensure the integrity of composite materials and protect the cement-based materials from external damages.

ACKNOWLEDGEMENT

General program of university natural science research of education department of Jiangsu, NO: (16KJB560011).

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